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Rees, Jr. et al.

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[54] **DOPANTS FOR SEMICONDUCTING MATERIALS**

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[21] Appl. No.: **08/889,972**

[22] Filed: **Jul. 10, 1997**

Related U.S. Application Data

[60] Provisional application No. 60/029,606, Oct. 24, 1996.

[51] **Int. Cl.**[7] **C07F 7/10**

[52] **U.S. Cl.** **556/410**; 556/404; 556/412; 564/511

[58] **Field of Search** 556/410, 412, 556/404; 564/511

[56] **References Cited**

U.S. PATENT DOCUMENTS

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[57] **ABSTRACT**

A magnesium amide for use as a magnesium donor not having any Mg—C bonds. The compound is useful for doping GaN with Mg^{+2}. The compound of the present invention is a high molecular weight dimer, preferably a diamide containing one or more silicon substituent groups. Alternatively, the compounds of the present invention may contain amino nitrogens weakly bonded to Mg. The compounds must have sufficient volatility to be useful in chemical vapor deposition.

16 Claims, No Drawings

DOPANTS FOR SEMICONDUCTING MATERIALS

This application claims priority from U.S. Provisional patent application Serial No. 60/029,606 filed Oct. 24, 1996.

FIELD OF THE INVENTION

The invention relates generally to dopants for semiconducting materials and, more particularly, to magnesium compounds suitable for making p-type gallium nitride (GaN).

BACKGROUND OF THE INVENTION

The preparation of blue light-emitting materials has become a heavily researched field in recent years. This interest is caused by the significant number of potential applications for blue light emitters. The two most commonly used light emitting devices (LED's) are liquid crystal displays (LCDS) and laser diodes. The two most technologically significant applications of blue LED's are electroluminescent displays and read/write heads for optical data storage. Full color electroluminescent red, green and blue (RGB) displays cannot be constructed because they are neither pure green nor pure blue LEDS.

Because the storage density increases inversely to the square of the light source wavelength, a blue LED laser-based optical data storage device, such as a CD-ROM, could store on the order of five times as much data as a standard red LED laser-based CD-ROM. This translates to about 3.25 Gbytes of data for a blue laser based CD, versus 650 Mbytes for the commonly used red laser based CDs. Another less obvious, significant, use of blue (or blue-green) LED's is in traffic signals. Traditional signals utilize a white incandescent light source with an appropriately colored glass filter. The use of an incandescent source, as well as a filter, yields a very inefficient device. The efficiency and longevity of traffic signals can be enhanced through the use of blue, LED's, as well as commonly available red and yellow LEDS. The energy cost savings and the lower maintenance requirements, when multiplied by the number of traffic signals in an average city, represent vast cost reductions. This approach is currently in use in Japan, where blue traffic signals, are used.

GaN and zinc selenide (ZnSe) have emerged as strong candidates for blue light-emitting materials; however, ZnSe suffers from short device lifetimes, relative to GaN. Furthermore, II–VI compounds are rather fragile and are grown at comparatively low temperatures. Thus, work has recently been expanding on GaN materials.

The thermodynamically stable phase of GaN at room temperature and atmospheric pressure is the hexagonal wurzite phase. This material is a direct bandgap semiconductor with a band gap of 3.45 eV. Light emitting diodes require a p-n junction. The fabrication of n-type GaN is not difficult, However, the fabrication of p-type GaN has presented challenges. Zinc has been used as a p-type dopant for GaN, however, its large size and propensity for forming covalent bonds have limited is usefulness. Magnesium has emerged as the dopant of choice for a p-type GaN. The most commonly utilized magnesium sources in the CVD (or MOMBE) growth of GaN:Mg have been organometallic compounds such as bis[cyclopentadienyl]magnesium (Cp_2Mg), bis[3(dimethyl)propyl]magnesium, and bis[3-(diethylamino)propyl]magnesium. The drawback of these sources is that they create a large carbon impurity (MgC) in the deposited GaN, which destroys the material's electronic

usefulness. To compensate for the detrimental effects of the carbon, two approaches have been used. The first is to apply several folds more Mg than needed. This, however, causes lattice deterioration, is expensive, and the devices burn out quickly. The second approach is to attempt to remove the carbon. To counter the formation of MgC, large quantities of H_2 have been injected into the reactor to form CH_4, which vaporizes. However, this in turn causes the formation of MgH_2, which also passivates the material.

SUMMARY OF THE INVENTION

The present invention is a magnesium donor designed to avoid the above problems. The compound is a volatile magnesium precursor lacking magnesium-carbon bonds. In its broadest sense, The invention encompasses all volatile Mg compounds not containing only Mg—C bonds. Since the final material, theoretically, places magnesium on a gallium site, a source material containing only magnesium-nitrogen bonds would seem most promising. The present invention, therefore, is a class of compounds useful for doping GaN with Mg. The compounds are volatile magnesium amides, not containing any Mg—C bonds. The most commonly prepared magnesium amide is tetrakis[bis (trimethylsilyl)amido]dimagnesium. This compound is a high molecular weight dimer. A more volatile, monomeric compound would be preferable for CVD applications. Optimally, the compounds are diamides containing one or more silicon groups. The compounds may contain amino-nitrogens weakly bound to Mg. The compounds must be volatile.

BRIEF DESCRIPTION OF THE DRAWINGS

This invention can be better understood with reference to the following drawings. The components in the drawings are not necessarily to scale, emphasis instead being placed upon clearly illustrating the principles of the present invention.

FIG. **1** is a thermogravimetric trace of $Mg[N(TMS)CH_2CH_2CH_2NMe_2]_2$.

FIG. **2** is a ball and stick depiction of the structure of $Mg[N(TMS)CH_2CH_2CH_2NMe_2]_2$.

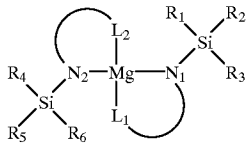
FIG. **3** is a depiction of the dative p-d bonding and metal disilylamides.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

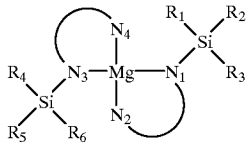
The invention is a class of compounds useful for depositing Mg^{2+} onto GaN. The compounds are magnesium amides having a sufficient volatility to be useful in chemical vapor deposition (CVD). The Mg is not bound to any carbons and is preferably bound only to nitrogen. However, a compound may fall within the bounds of the invention if it has one hydrogen or alkyl-Mg bond if the compound is sufficiently volatile. In other words, compounds such as $HMgNR_1R_2$ and $R_3MgNR_1R_2$, where R_1, R_2, or R_3 represent alkyl, are included in the invention if they have sufficient volatility.

Preferably, the compounds are diamides, having two amide groups connected to the Mg. Most preferably, the compounds are four—coordinate diamides, having two Mg—N amide bonds and two Mg—N bonds from tertiary amines. Also, most preferably, at least one of R_1 or R_2 is a silicon substituent. The compounds should have a vapor pressure of about 10^{-2} torr at 100° C.

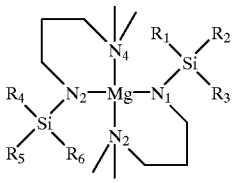
In a preferred embodiment, the compounds have the general structure:



wherein L_1 and L_2 are not C. More preferably, the compounds have the general structure:



wherein R_1–R_6 are alkyl. One compound of the general structure has been synthesized and characterized, having the structure:



Magnesium bis-[γ-dimethylaminopropyl) trimethylsilylamide], 200 FIG. **2**, was prepared by the reaction of the free amine with dibutylmagnesium in hexane. It is a white solid at ambient conditions and has been shown to be a monomer in the solid state by single crystal x-ray diffraction. The compound is volatile, as demonstrated by its thermogravimetric trace 100 (FIG. **1**), and can be sublimed at 80° C. and 0.01 Torr. The compound, like most other group 2 element amides, is quite air sensitive.

Single crystals of the compound were obtained by slow sublimation. A crystal of suitable quality for x-ray diffraction was selected and mounted in a glass capillary in an inert atmosphere glove box. The unit cell was determined from 25 centered reflections with 2θ values between 20° and 35°. Unit cell data and collection parameters are given in Table 1. The magnesium atom is tetrahedrally bonded to four nitrogen atoms; two from amide bonds and two from coordinate covalent bonds to tertiary amines (FIG. **2**). The amide nitrogen atoms are planar, indicating an sp^2 hybridization, due to dative bonding from the full nitrogen p-orbital to the empty silicon d-orbital 300, as shown in FIG. **3**. Interatomic distance and angle data is given in Tables 2 and 3.

N-(γ-dimethylaminopropyl)trimethylsilylamine 200. Under argon, in a 500 ml Schlenk flask containing a magnetic stir bar, 49.38 g (0.480 mol) of 3-dimethylaminopropylamine (99%, Aldrich) was added to 120 ml of anhydrous hexanes (distilled from Na). This mixture was stirred and cooled with a constant temperature bath at 10° C. From a dropping funnel, 25 g of TMS-Cl (0.230 mol) were added dropwise to the mixture over a period of two hours. A white precipitate formed, and later redissolved forming a separate layer at the bottom of the flask. Once the TMS-Cl addition was complete, 200 ml of anhydrous ether (distilled from Na/K) was added to the flask. The mixture then was rapidly stirred overnight causing the two layers to merge into a homogeneous solution over a white precipitate. The solution was separated from the white solid by cannulation and distilled at ambient pressure to give TMS-NH—$CH_2CH_2CH_2NMe_2$ at 160° C. Yield: 85%. Characterization: ^1H NMR: (400 MHz, positive δ downfield referenced to $Si(CH_3)_4$=0 ppm utilizing residual $CDCl_3$= 7.24 ppm in solvent $CDCl_3$) 2.72 [m, 2H, —CH_2NMe_2], 2.24 [m, 2H, TMS-NH—CH_2—], 2.20 [s, 6H, —NCH_3], 1.54 [m, 4H, TMS-NH—CH_2CH_2—], 0.02 [s, 18H, CH_3Si—]. $^{13}C\{^1H\}$ NMR: (75 MHz, positive δ downfield referenced to $Si(CH_3)_4$=0 ppm utilizing residual C_6D_5H= 128.0 ppm in solvent C_6D_6) 57.45 [—CH_2NMe_2], 45.40 [—NCH_3], 40.00 [TMS-N—CH_2—], 32.66 [TMS-N—CH_2CH_2—], –0.20 [$(CH_3)_3Si$—N—]. Mass Spectrum: (EI, 70 eV) 174 [TMS-$NHCH_2CH_2CH_2NMe_2]^+$, 159 (M—Me), 129, 114, 100, 85, 72, 58.

Magnesium bis[N-(γ-dimethylaminopropyl) trimethylsilylamide]. (FIG. **2**) In a 100 ml Schlenk flask equipped with a magnetic stir bar and argon purge were combined 4.46 g of N-(γ-dimethylaminopropyl) trimethylsilylamine and 10 ml of anhydrous THF (twice distilled from Na). The contents of the flask were stirred and cooled to –10° C., then 12 ml of $MgBu_2$ (1M solution in heptane) were added slowly by syringe over a period of two minutes. The solution was allowed to warm to room temperature and then was heated to reflux for 5 hours. The flask was allowed to cool to room temperature. The THF was removed under vacuum leaving an off-white solid. The solid was sublimed at 80° C. and 10^{-4} mm Hg to yield purified $Mg(N\{TMS\}CH_2CH_2CH_2NMe_2)_2$ as a crystalline, white solid. Yield: 52%. Characterization: Mp 106° C. TGA: (FIG. **1**) Onset of weight loss, 141° C.; 1.2% residue at 500° C. $^{29}Si\{^1H\}$ NMR: (79.5 MHz, in C_6D_6, positive δ downfield referenced to $Si(CH_3)_4$=0 ppm) –8.16 [$SiMe_3$]. ^1H NMR: (400 MHz, positive δ downfield referenced to $Si(CH_3)_4$=0 ppm utilizing residual C_6D_5H=7.15 ppm in solvent C_6D_6) 3.41 [m, 2H, —$CH_{2(a)}NMe_2$], 3.03 [m, 2H, —$CH_{2(b)}NMe_2$], 2.15 [s, 6H, —$NCH_{3(a)}$], 2.05 [m, 4H, TMS-N—CH_2CH_2—], 1.71 [s, 6H, —$NCH_{3(b)}$], 1.57 [m, 2H, TMS-N—$CH_{2(a)}$—], 1.28 [m, 2H, TMS-N—$CH_{2(b)}$—], 0.49 [s, 18H, $(CH_3)_3Si$—]. $^{13}C\{^1H\}$ NMR: (100 MHz, positive δ downfield referenced to $Si(CH_3)_4$=0 ppm utilizing residual C_6D_5H=128.0 ppm in solvent C_6D_6) 62.91 [—CH_2NMe_2], 49.11 [TMS-N—CH_2—], 47.78 [—$NCH_{3(a)}$], 45.82 [—$NCH_{3(b)}$], 32.70 [TMS-N—CH_2CH_2—], 2.37 [$(CH_3)_3$ Si—N—]. Mass Spectrum: (EI, 70 eV) 370.3 [$Mg(N\{TMS\}CH_2CH_2CH_2NMe_2)_2]^+$, 353.2, 324.4, 306.3, 277.3, 250.3, 196.2, 174.2, 159.2, 146.1, 129.1, 114.1, 100.1, 85.1, 73.1, 58.1. Elemental Analysis: Calculated: C, 51.9%; H, 11.4%; N, 15.1%. Found: C, 52.0%; H, 12.5%; N, 15.2%.

TABLE 1

Unit cell and data collection parameters.

Empirical Formula	$MgC_{16}H_{42}N_4Si_2$
Formula Weight	371.01 g/mol.
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal System	monoclinic
Space Group	$P2_1/n$
Unit Cell Dimensions	a = 10.188(2) Å b = 16.401(5) Å β = 101.79(3)° c = 15.208(7) Å
Volume	2487.6(15) $Å^3$
Z	4
Density (calc'd)	0.991 g/cc
Absorption Coefficient	0.17 mm^{-1}
F(000)	824.94

TABLE 1-continued

Unit cell and data collection parameters.

θ Range for Data Collection	2.29° to 25°
Index Ranges	−12 ≦ h ≦ 11, 0 ≦ k ≦ 19, 0 ≦ 1 ≦ 18
Reflections Collected	4771
Independent Reflections	4360
Refinement Method	Full-matrix least-squares on F^2
Data/Restraints/Parameters	1793/0/208
Goodness of Fit on F^2	2.45
Final R Indices [I > 2σ(I)]	R = 0.079, R_w = 0.085
R Indices (all data)	R = 0.163, R_w = 0.096
Largest Difference Peak and Hole	0.340 and −0.180 e/Å^3

TABLE 2

Interatomic distances.

Atoms	Distance(Å)	Atoms	Distance(Å)
MG-N1	1.979(7)	N1-C1	1.495(12)
MG-N2	2.189(8)	N2-C3	1.459(17)
MG-N3	1.969(7)	N2-C4	1.482(15)
MG-N4	2.212(8)	N2-C5	1.442(17)
SI1-N1	1.668(7)	N3-C9	1.503(14)
SI1-C6	1.835(12)	N4-C11	1.437(19)
SI1-C7	1.853(12)	N4-C12	1.418(17)
SI1-C8	1.859(10)	N4-c13	1.427(18)
SI2-N3	1.682(7)	C1-C2	1.463(18)
SI2-C14	1.874(11)	C2-C3	1.537(23)
SI2-C15	1.872(12)	C9-C10	1.493(23)
SI2-C16	1.820(12)	C10-C11	1.51(3)

TABLE 3

Interatomic angles.

Atoms	Angle (°)	Atoms	Angle (°)
N1-MG-N2	97.0(3)	MG-N2-C3	113.6(7)
N1-MG-N3	137.6(3)	MG-N2-C4	106.4(6)
N1-MG-N4	105.5(3)	MG-N2-C5	113.0(7)
N2-MG-N3	107.1(3)	C3-N2-C4	115.1(9)
N2-MG-N4	111.8(3)	C3-N2-C5	104.9(10)
N3-MG-N4	97.4(3)	C4-N2-C5	103.5(10)
N1-SI1-C6	112.6(5)	MG-N3-SI2	130.2(4)
N1-SI1-C7	111.3(5)	MG-N3-C9	115.8(6)
N1-SI1-C8	111.1(4)	SI2-N3-C9	114.0(6)
C6-SI1-C7	105.4(6)	MG-N4-C11	114.5(8)
C6-SI1-C8	108.8(6)	MG-N4-C12	114.8(8)
C7-SI1-C8	107.3(5)	MG-N4-C13	105.8(7)
N3-SI2-C14	111.7(4)	C11-N4-C12	106.2(13)
N3-SI2-C15	113.4(5)	C11-N4-C13	112.6(12)
N3-SI2-C16	111.4(4)	C12-N4-C13	102.5(13)
C14-SI2-C15	104.9(6)	N1-C1-C2	116.5(9)
C14-SI2-C16	108.5(6)	C1-C2-C3	115.8(11)
C15-SI2-C16	106.4(5)	N2-C3-C2	112.6(10)
MG-N1-SI1	128.3(4)	N3-C9-C10	116.8(10)
MG-N1-C1	116.9(5)	C9-C10-C11	115.1(12)
SI1-N1-C1	114.8(6)	N4-C11-C10	114.4(13)

TABLE 4

Atomic coordinates.

Atom	x	y	z
MG	0.85598(23)	0.34056(14)	0.19779(15)
SI1	1.08267(25)	0.46996(16)	0.30000(18)
SI2	0.68260(29)	0.32077(17)	0.35870(18)
N1	1.03505(65)	0.39205(39)	0.23031(43)
N2	0.92555(94)	0.21749(46)	0.17523(55)

TABLE 4-continued

Atomic coordinates.

Atom	x	y	z
N3	0.69597(65)	0.32860(44)	0.25060(45)
N4	0.75620(88)	0.39939(58)	0.07076(50)
C1	1.14391(99)	0.35599(72)	0.18994(79)
C2	1.16103(122)	0.26754(86)	0.19764(105)
C3	1.04893(168)	0.21620(73)	0.14057(92)
C4	0.93137(158)	0.17209(69)	0.26023(84)
C5	0.83008(149)	0.17175(71)	0.11077(101)
C6	1.18284(129)	0.54536(76)	0.25351(99)
C7	1.19092(119)	0.43522(93)	0.40649(73)
C8	0.93533(100)	0.52203(58)	0.32934(67)
C9	0.56473(109)	0.32078(88)	0.18474(90)
C10	0.53485(125)	0.38379(109)	0.11251(107)
C11	0.61756(172)	0.37769(112)	0.04093(111)
C12	0.81851(191)	0.38511(122)	−0.00308(90)
C13	0.77494(191)	0.48495(91)	0.08512(94)
C14	0.59022(163)	0.22617(80)	0.37928(80)
C15	0.58646(123)	0.40651(79)	0.39686(81)
C16	0.84655(119)	0.31997(71)	0.43364(66)

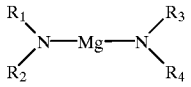
What is claimed is:

1. A magnesium dopant compound for use in depositing electronic materials and the like comprising a volatile magnesium amide with Lewis acid bonding sites occupied by elements or compounds selected from the group consisting of nitrogen atoms and alkyl groups.

2. A magnesium donor compound for use as a dopant comprising:

a volatile magnesium precursor having cationic bonding sites occupied by amide groups and at least one silicon substituent, said compound having a vapor pressure of around $10^{(-2)}$ torr at 100° C.

3. A magnesium amide having a vapor pressure of at least 1×10^{-5} Torr at 200° C., the magnesium amide having the formula



Wherein

R_1, R_2, R_3, R_4 are independently selected from the group consisting of C_{1-10} alkyls, C_{6-16} aryls, C_{3-8} cycloalkyls, C_{1-10} unsaturated alkyls, polyaryl moieties of 2–3 aryl rings, C_{1-10} aralkyl, C_{1-10} alkaryl, substituted or unsubstituted heteroatom derivatives thereof wherein the heteroatom is selected from the group consisting of O, N, Si, S, and P, and the substituents are selected from the group consisting of halogens, halogenated alkyls of C_{1-10}, and alkyls of C_{1-10}, trialkylsilyl or dialkylsilyl wherein the alkyl substituent is C_{1-10}, provided that if R_1, R_2, R_3, R_4 each are trialkylsilyl, at least one of R_1, R_2, R_3, or R_4 must have at least one alkyl group containing a β hydrogen.

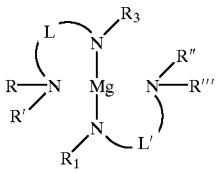
4. The compound of claim **3** wherein R_1=R_3 and R_2=R_4, the magnesium amide is homoleptic.

5. The compound of claim **4** wherein R_1=R_3=trialkylsilyl or dialkylsilyl.

6. The compound of claim **4** wherein R_2=R_4=substituted or unsubstituted heteroatom derivatives, wherein the heteroatom is N.

7. The compound of claim **6** wherein the substituents are selected from the group consisting of alkyls of C_{1-10}.

8. A magnesium amide as set forth in claim **3** selected from the group consisting of



wherein R_1 and R_3 are independently selected as defined in claim **1**, and R, R', R" and R'" are independently selected from the group consisting of alkyls of C_{1-10}, and L and L' are independently selected from the group consisting of substituted or unsubstituted heteroatom derivatives of C_{1-10} alkylenes, C_{6-10} arylenes, C_{3-8} cycloalkylenes, or C_{1-10} unsaturated alkylenes, polyarlyene moieties of 2–3 aryl rings, C_{1-10} aralkylene, C_{1-10} alkarylene, wherein the heteroatom is selected from the group consisting of O, N, Si, S and P, and the substituents are selected from the group consisting of halogens, halogenated alkyls of C_{1-10}, alkyls of C_{1-10}, and trialkylsilyl or dialkylsilyl units, wherein the alkyl substituents are C_{1-10}.

9. The compound of claim **8** wherein R=R'=R"=R'".

10. The compound of claim **8** wherein R_1=R_3.

11. The compound of claim **9** wherein R_1=R_3.

12. The compound of claim **11** wherein L=L'.

13. The compound of claim **11** wherein L=L'=saturated alkylene of C_{1-10}.

14. The compound of claim **8** wherein R, R', R", R'" are independently selected from the group of C_{1-4} saturated alkyls.

15. The compound of claim **14** wherein R=R'=R"=R'".

16. The compound of claim **8** wherein R_1, and R_3 are independently selected from the group of trialkylsilyl or dialkylsilyl substituents, with the alkyl being of C_{1-4} saturated.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 6,156,917
DATED : December 5, 2000
INVENTOR(S) : William S. Rees, Jr and Henry A. Luten, III

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 1, line 56, after "difficult", delete the "," and replace with --.--

Column 2, line 15, delete the word "The" and replace with --the--.

Column 2, line 61, delete the phrase "four–coordinate" and replace with --four coordinate--.

Column 3, lines 22-31, in the structure disclosed, delete the atom "N_2" immediately to the left of "Mg", and replace with --N_3-- .

Column 6, line 35 (claim 3), after "C", delete the ".".

Signed and Sealed this

Twenty-ninth Day of May, 2001

Attest:

Nicholas P. Godici

NICHOLAS P. GODICI

Attesting Officer

Acting Director of the United States Patent and Trademark Office